THE MICROWAVE SPECTRUM, STRUCTURE, AND DIPOLE MOMENT OF THIONYL FLUORIDE[1]

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Abstract

The microwave spectrum of thionyl fluoride, SOF_2, from 16,900 to 36,000 mc. has been recorded, and approximately thirty pure rotational transitions identified. The reciprocal moments of inertia fitting the $S^{32}O^{16}F^{19}_2$ spectrum are $\underline{a}$ = 8614.75 mc., $\underline{b}$ = 8356.98 mc., $\underline{c}$ = 4952.96 mc., and those for the $S^{32}O^{18}F^{19}_2$ spectrum are $\underline{a}$ = 8582.33 mc., $\underline{b}$ = 7843.37 mc., $\underline{c}$ = 4777.90 mc. The structural parameters fitting these moments are: $r_{SO} = 1.412 \pm 0.001$ Å, $r_{SF} = 1.585 \pm 0.001$ Å, $\angle FSF = 92°49' \pm 5'$, $\angle OSF = 106°49' \pm 5'$. Stark effect measurements give a dipole moment of 1.618 ± 0.010 debye unit along an axis $38°50' \pm 30'$ from the SO bond and $80°23' \pm 30'$ from the SF bond.

(1) This work was supported by the Navy Department through the ONR under Task Order V of Contract N5ori-76.

The closely related compounds thionyl fluoride, SOF_2, and sulfuryl fluoride, SO_2F_2, are ideal for the study of the effect of strongly electronegative substituents on the adjacent sulfur-oxygen bond. The analysis of the microwave spectrum of sulfuryl fluoride gave structural parameters which definitely disagreed with the electron diffraction results,[2] the most noteworthy feature of

(2) R. M. Fristrom, J. Chem. Phys., 20, 1 (1952).

the microwave structure being an unusually short S-O bond distance. The present work was undertaken to determine whether a shortening of the S-O bond would be observed in thionyl fluoride. This compound has also been studied by the electron diffraction method, but the results have not been reported in full.[3]

(3) D. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," p. 307, Prentice-Hall (1946).

Experimental

Preparation of Thionyl Fluoride

The $S^{32}O^{16}F^{19}_2$ sample was prepared by reacting thionyl chloride with antimony trifluoride in the presence of antimony pentachloride.[4] The product

(4) This sample was prepared by Dr. J. K. O'Loane, who kindly furnished a portion of his product for the microwave study. See J. K. O'Loane and M. K. Wilson, "The Infrared Spectrum of Thionyl Fluoride," to be published.

was purified by shaking over mercury and by repeated distillation until the vapor pressure and the infrared spectrum showed no further change.

The $S^{32}O^{18}F^{19}_2$ sample was prepared from an oxygen sample enriched to about 23 atom percent in the O^{18} isotope.[5] A small volume of this oxygen was heated

(5) The oxygen sample was furnished by Prof. Alfred O. C. Nier of the University of Minnesota, where the isotopic separation was made possible by a grant from the Committee on Growth of the National Research Council acting in behalf of the American Cancer Society.

over an excess of sublimed sulfur and the resulting sulfur dioxide was converted to thionyl fluoride by reaction with argentous fluoride at 200°C. Due to the small volume of sample, no extensive purification of the product was undertaken. The only impurities present in more than trace amounts, as indicated by the infrared spectrum, were unreacted sulfur dioxide and some silicon tetrafluoride formed by the reaction of argentous fluoride with the glass system. Silicon tetrafluoride does not absorb in the microwave region, and sulfur dioxide was known to have no absorption lines in the region of particular interest for this work.

Observed Spectrum

A Stark modulation microwave spectrograph[6] was employed to measure the

(6) K. B. McAfee, R. H. Hughes, and E. B. Wilson, Jr., Rev. Sci. Instr., 20, 621 (1949).

absorption lines of the gas between 16,900 and 36,000 megacycles/second. All frequencies were measured with a crystal-driven frequency standard calibrated against the 5 mc. signal from station WWV. The frequencies reported are believed to be accurate to 0.1 mc.

Approximately 130 absorption lines were observed in the region of the spectrum covered. Quantitative measurements of the Stark effects of several lines were made for identification purposes and for dipole moment calculations.

The zero-based square wave generator and the waveguide were calibrated by measuring the Stark lobes of the $J = 1 \rightarrow 2$ transition of $O^{16}C^{12}S^{32}$ in the ground vibrational state and using the dipole moment given by Shulman and Townes[7] for the calculation of the electric field strengths.

(7) R. Shulman and C. H. Townes, Phys. Rev., 77, 500 (1950).

ANALYSIS OF SPECTRUM

$S^{32}O^{16}F^{19}_2$ Transitions

The analysis was aided by a rough prediction of the spectrum from the electron diffraction data. Since the molecule is pyramidal and asymmetric, the dipole moment is not constrained to lie along a principal axis, and transitions associated with its components along the two axes in the symmetry plane may occur.

Three $J = 1 \longrightarrow 2$ pure rotational transitions near 34,000 mc. were identified by means of their Stark effects and were assigned as the $\Delta K_{-1} = 1$, $\Delta K_1 = 0$ type.[8] Three other lines at somewhat lower frequencies were identified

(8) The notation of G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys., 11, 27 (1943), is used.

as the type $J = 1 \longrightarrow 2$, $\Delta K_{-1} = 0$, $\Delta K_1 = 1$. The latter transitions were considerably weaker, and a detailed study of their Stark patterns was hindered by the presence of several stronger lines. However, the Stark effects observed for these lines were qualitatively correct. The identifications were confirmed when the assignment of three of the lines yielded reciprocal moments of inertia which correctly predicted some twenty-odd additional pure rotational transitions (Table 1).

$S^{32}O^{18}F^{19}_2$ Transitions

[illegible] of S^{34} is about 4 per[illegible], none of the observed lines could be identified as arising from the [illegible] species. In order to determine the structure of thionyl fluoride, it was necessary to prepare an isotopic sample. The O^{18} isotope was chosen because substitution far from the molecule's center of mass was to be preferred.

Estimates of the frequencies of the $S^{32}O^{18}F^{19}_2$ transitions could be made from the spectrum of the normal isotopic species. The three stronger J = 1 ⟶ 2 transitions were readily found and identified by a detailed study of their Stark effects. The moments of inertia for the new isotopic species were calculated and found to be consistent with the moments for the normal species (Table 2).

After the molecular structure had been determined as described below, the final model was used to predict the stronger J = 1 ⟶ 2 transitions of $S^{34}O^{16}F^{19}_2$. An estimate placed their intensities near the lower limit of sensitivity of the spectrograph. The lines were apparently too weak to be observed under the conditions used, for none of them were found.

STRUCTURAL PARAMETERS

The observed microwave spectrum is consistent with the pyramidal structure assigned by the electron diffraction work, except that the identification of two of the principal axes must be changed. The two types of transitions observed require the a and c axes, i.e., the axes having the least and greatest moments of inertia, to lie in the symmetry plane of the molecule. The electron diffraction model placed the b and c axes in the symmetry plane; the interchange of the a and b axes indicate that the angles reported [illegible]

The frequencies of the transitions which would occur if the dipole had a non-zero component along the intermediate axis were calculated, but none of these transitions were observed. The absence of [illegible] transitions indicates [illegible] the b-component of the dipole moment must be small [illegible] and this [illegible] to support the assumption that the two S-F distances are equal.